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<b>EP-A- 0 038 126</b>	<b>EP-A- 0 039 617</b>
<b>DE-A- 2 300 206</b>	<b>DE-A- 3 426 870</b>
<b>GB-A- 1 563 190</b>	<b>US-A- 4 501 830</b>

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## Description

The invention relates to cementitious compositions and products made from such compositions. More particularly, the invention relates to substantially clay-free compositions comprising a hydraulic cement, water, a water-soluble polymer and a cross-linking agent for said polymer. It is to be understood that the compositions according to this invention are substantially clay-free.

By the term "reactive water-soluble polymer" in this specification is meant any water-soluble or water dispersible polymer or mixture of such polymers which can be reacted with an appropriate cross-linking agent to cause the polymer to become insoluble, or substantially so, in products made from the cementitious compositions of this invention.

By the term "hydraulic cement" in this specification, there is meant any material which sets and hardens by the addition of water, that is in the presence of water. The hydraulic cement may, for example, be a silicate cement such as Portland cement or it may be an aluminate cement. The term includes mixtures of two or more different hydraulic cements.

In making cementitious products, it is desirable that the resultant product should be of high strength and especially high flexural strength.

This is particularly important when the products are to be used as building products, for example roofing slates, and for use in such applications it is desirable that the products should not only have a flexural strength of at least 15 MPa and advantageously 40 MPa, but also good durability, i.e. good resistance to:

- a) variations in climatic conditions particularly freeze-thaw conditions and cycles of alternate rain and sunshine;
- b) ultra-violet attack;
- c) acid rain; and,
- d) abrasion of surfaces by the elements

such that the strength of the building product is maintained satisfactorily throughout its life.

Cementitious products produced from an hydraulic cement paste consisting of hydraulic cement and water only generally have low strength, especially low flexural strength, and poor durability. For example, a product formed from a cementitious composition which comprises an ordinary hydraulic cement with a typical spread of particle size range and an amount of water which is conventionally used in such compositions may have a flexural strength as low as 5 to 10 MPa. Moreover unless substantial amounts of aggregate (i.e. sand or crushed rock or the like) are incorporated into such cementitious products they will not normally be durable in natural weathering conditions.

Various proposals have been made for improving the strength of such cementitious compositions. For example, it is known that the flexural strength and/or impact strength of a product formed from such a composition may be improved by including a fibrous material in the composition. Such fibre-reinforced-cement pastes are also sometimes acceptably durable in natural weathering conditions, the best known example being asbestos-cement products.

Fibrous materials which have been used in the past to increase the flexural strength of cementitious products include fibres of asbestos, glass, steel, ceramic, polymeric and vegetable materials. The use of such fibres does, however, have certain disadvantages. The flexural strength of products made from compositions including such materials may be appreciably increased to a figure of the order of 40 MPa in the short and medium terms; however, in the long term the presence of the fibrous material may not be entirely satisfactory because fibres may suffer degradation due to alkali attack, which coupled with long term weathering may also adversely affect the durability of the finished product. Moreover, the use of such fibres may add to the difficulty of processing the cementitious composition and in the case of some fibres, for example, asbestos, may involve health hazards.

A number of proposals have also been made for improving the strengths of cementitious products. For example, capital intensive high pressure forming, compaction and vibration apparatus may be employed to produce products having low porosity and high flexural strength. Such proposals have been utilised for forming products from cement pastes, mortars and ceramic materials. A further proposal involves the addition of processing aids to the composition which enables the elimination, to a great extent, of voids in products made from such compositions. The only processing aids which have been found to be suitable for this purpose are water-soluble polymers and proposals for their use have been made particularly in the case of compositions having a low water/cement ratio, for example, below 30 parts by weight of water per 100 parts of the hydraulic cement. Examples of polymers which have been described in the prior art as processing aids include especially cellulose ethers and also polyacrylamides and hydrolysed polyvinyl acetates. Proposals for using such processing aids have described using up to 25% by weight of the processing aid in a cement/water composition.

Examples of published Patent Specifications describing cementitious compositions and products of the above type are British Patent Specification No. 1563190 and the following European Patent Specifications 0021681, 0021682, 0030408,

0038126, and 0055035.

A large number of the compositions described in these patent specifications suffer from the drawback that they include a relatively large proportion of the processing aids.

It is believed that the improved micro-structure and increase in strength of products made from such compositions results in part from the effect of the polymers on the rheology of the composition. However, it has been proposed that, in cured or hardened products obtained from the compositions, the polymers act as an adhesive between the cementitious entities of the composition. The strength of the bond provided by the polymer adhesive, however, depends, amongst other factors, upon the water content of the composition. Ultimately, therefore, there will be a complete loss of strength because the polymer may re-dissolve or otherwise become less effective if sufficient water is available. Thus, a number of the compositions described in the specifications listed above, while possessing relatively high initial flexural strength when dry, do not have adequate strength when wet or adequate durability for use as building products. This has been demonstrated for the products made from such compositions by the marked decrease in flexural strength when tested under conditions simulating those experienced by building products, for example in water absorption tests or tests involving repeated freezing and thawing of the products and tests involving repeated wetting and drying.

In DE-A-2 300 206 there is disclosed curable composition comprising in admixture a hydraulic cement, a filler, water, an organic polyisocyanate and an isocyanate reactive water-soluble polymer in an amount sufficient to ensure that, after mixing, the composition remains compatible with, and dispersible by, water until the composition has cured to the point of initial set. The water-soluble polymers which can be used include derivatives of cellulose, for example, various cellulose ethers including methyl cellulose and hydroxy ethyl cellulose. The composition may also include one or more other isocyanate reactive organic compounds additional to the water-soluble polymer, and such compounds may be epoxy compounds. In contrast to the uses of the present invention, DE-A-2 300 206 is concerned with cement compositions which are suitable for surfacing floors, walls and the like and the invention is designed to give an early initial set.

It is essential that the compositions of the present invention do not contain an isocyanate and compositions containing isocyanates are disclaimed from the claims of this invention.

We have found that products with relatively small amounts of water-soluble polymer are less susceptible to attack by water, i.e. the hardened

composition has a low strength when saturated with water compared to the strength thereof in the dry state, or such products may also suffer gradual loss of strength during exposure to water or they will break down when subjected to freeze-thaw conditions even though such products are superior to those taught by the prior art.

We have now found surprisingly that significant improvement in strength can be obtained by the use of a cross-linking agent in conjunction with a reaction water-soluble polymer.

Accordingly, the present invention provides an uncured cementitious composition which is free of isocyanates comprising in admixture:-

- (a) at least one hydraulic cement;
- (b) at least one reactive water-soluble polymer which is capable of providing a viscous solution in water at low addition levels as hereinbefore defined;
- (c) water in an amount of from 10 to 25 parts by weight of water per 100 parts by weight of the cement; and
- (d) a water soluble cross-linking agent capable of effecting chemical cross-links between molecules of the said polymer in the presence of the cement and water.

The water-soluble polymer is preferably capable of giving a viscosity exceeding 50 cps as a 5.0% solution by weight in water. Also it is preferred that the composition contains from 0.2, and more preferably 0.5 to 5 parts by weight of the water-soluble polymer per 100 parts per weight of the cement.

The water-soluble polymer to be used in the practice of this invention has to be reactive so that the cross-linking agent is able to react with the molecules of the polymer to insolubilise the polymer by forming the cross-links. It will be appreciated that a cross-linking agent which is very reactive with water is unsuitable for this purpose.

In the present invention the susceptibility to water is overcome by the use of the cross-linking agent, rendering the polymer insoluble in water and reducing the absorption of water and loss of strength of the products. Further benefits that may be derived from the addition of such cross-linking agents are (a) modifications to rheology of the mix which may assist in processing, (b) the formation of chemical links between two or more polymers used simultaneously in the mix, (c) formation of chemical links between the polymer and a fibrous reinforcement such as cellulose fibres, (d) a shortening of the time required to harden and develop strength in the cementitious composition, particularly when hot pressing is employed as the shaping method for the final product, and (e) formation of chemical bonds between cement and polymer.

In order for the polymer to fulfil the above

functions a uniform concentration of polymer in the cement must first be obtained. It is known that cellulose ethers can give inhomogeneous aqueous solutions which can be overcome by partial cross-linking to delay or eliminate solubility. An alternative method to delay solubility and obtain a uniform solution is to predisperse the polymer in a weak solvent which is also miscible with water. An example would be polyacrylamide predispersed in alcohol. Lower water content cement systems at high polymer concentration can be prepared in accordance with this invention using a weak solvent which would not be possible by standard dissolution techniques.

However, if the polymer cross-linking reaction proceeds too rapidly for full dispersion a non-uniform concentration of cross-linked polymer is obtained and this results in a product which does not have the desired properties. An example of this would be the reaction of polyacrylamide with glyoxal at temperatures between 15° and 30° C. Thus, it is also a feature of the present invention that cross-linking may proceed at a rate which allows complete uniform dissolution of the polymer in the cementitious mixture.

Cross-linking of water-soluble polymers can be achieved by condensation with difunctional reagents, free radical reaction at unsaturated carbon-carbon double bonds, and complexing reagents with polyvalent ions. These mechanisms can be illustrated by the behaviour of cellulose ethers as described below.

Cross-linking of cellulose ethers may be accomplished by condensation reaction through hydroxol groups. Under the alkaline conditions which exist during the mixing and hardening process for most hydraulic cements we have found that this reaction can be carried out with, for example;

- a) labile chlorine reagents
- b) sulphones
- c) epoxides

Alternatively, cellulose ethers may be modified so that they can be cross-linked by a free radical mechanism. For example, modification can be introduced by reaction with allyl halides to introduce unsaturation which then serves as an active site for reaction which can be initiated later. Hydroxypropylmethyl cellulose can be reacted with acrylamide monomers, such as methylene bis-acrylamide at around 70° C in alkaline conditions to form a water insoluble cross-linked polymer. Also, cross-linking reagents can be chosen that react only at elevated temperatures with the polymer, do not alter the characteristics of the forming process, and are compatible with the other stages of processing such as hot pressing.

Accordingly, in practising the invention the re-

active water-soluble polymer and the water-soluble cross-linking agent preferably, consist of at least one of the following pairs:-

- (a) a cellulose ether plus a diepoxide;
- (b) a cellulose ether plus a sulphone;
- (c) a cellulose ether plus a compound containing labile chlorine;
- (d) a cellulose ether plus ethylene imine;
- (e) a carboxycellulose ether with polyvalent cation;
- (f) polyacrylamide, or a derivative thereof or a copolymer of acrylamide plus a dialdehyde;
- (g) polyvinylalcohol or partially hydrolysed polyvinylacetate plus an inorganic acid;
- (h) gelatin plus formaldehyde;
- (i) polyacrylic acid or polyacrylic acid salt plus diepoxide;
- (j) a cellulose ether plus an acrylamide monomer, and a free radical initiator or heat;
- (k) an allyl substituted cellulose ether plus a free radical initiator or heat.

With regard to the reactive water-soluble polymer and the water-soluble cross-linking agent, it is preferred that the cellulose ether is a hydroxypropyl methyl cellulose and the diepoxide is 1,4 butanediol diglycidyl ether, or butadiene diepoxide, or the diglycidyl ether of 1,2,3 propane triol, or vinylcyclohexanone dioxide together with zinc fluoroborate as catalyst. When the water-soluble polymer is polyacrylamide, it is preferred that the dialdehyde is glutaraldehyde or glyoxal. When the water-soluble polymer is polyacrylamide it is preferably dissolved in a volatile, water-miscible solvent prior to mixing with the hydraulic cement.

Further, it is preferred that the water-soluble polymer is hydroxypropylmethyl cellulose the sulphone is bis(2-hydroxyethyl) sulphone, or alternatively in place of the sulphone the cross-linking agent is ethylene imine. Another combination to be used in accordance with this invention is when the cellulose ether is hydroxypropylmethyl cellulose the cross-linking agent is one with labile chlorine, preferably dichloropropanol or epichlorohydrin. An alternative cellulose ether which may be used in practicing the present invention is hydroxy ethyl cellulose, although other cellulose derivatives may be used including sodium carboxymethyl cellulose.

In a further aspect of the invention the water-soluble polymer may be polyvinyl alcohol, or a partially hydrolysed polyvinyl acetate.

In another form of the invention, the cellulose ether is hydroxypropylmethyl cellulose and the acrylamide monomer is methylene bis-acrylamide.

The water soluble polymer may be allyl substituted cellulose ether, such as acrylamido methylated cellulose and the free radical initiator may be potassium persulphate or nitrile N-oxide. Alternatively the allyl substituted cellulose ether may be

allyl hydroxypropylmethyl cellulose and the free radical initiator may be potassium persulphate with sodium bisulphate.

The cementitious composition according to the present invention may contain, in addition to the cement, water and processing aid, other materials known in art. For example these materials may include fibrous materials, fine fillers, dispersants and chemical modifiers which modify the setting ability of the composition. The fillers and/or aggregates may include slate dust, various forms of sand and the like and these may be mixed with pigments in order to give the finished product a preferred colour. The cementitious composition may furthermore comprise blast furnace slag or pulverised fuel ash or a natural or artificial pozzolana.

In particular it is preferred to include 5 to 20 parts by weight of cement of fine silica particles having a particle size distribution substantially between 0.005 microns (50 Å) and 0.5 microns, and known variously as silica fume micro-silica or colloidal silica, because of the further improvement in durability which is thereby effected.

The constituents of the cementitious composition are desirably subjected to high shear mixing in order to plasticise the composition and convert it to a smooth paste or a material of dough-like consistency. The high shear mixing may be achieved, for example, in a Z-blade mixer or a twin-roll-mill. The paste or dough-like material is then compressed and maintained under pressure in order to remove substantially all of the larger voids in the material. Alternatively, it is sometimes advantageous to mix the particulate ingredients of the cementitious composition in some form of planetary mixer, for example, before adding the liquid ingredients during a second high shear mixing process under vacuum, for example in a vacuum extruder when the need to press for extended periods is thereby eliminated.

It is to be understood therefore that the invention also includes a method of making a cementitious composition wherein the specified ingredients (a), (b), (c) and (d) are mixed under conditions of high shear to produce a uniform composition and to remove all or substantially all of the voids from the composition and to convert the composition into a material of dough like consistency. It is preferred that a material of dough like consistency is such that after hardening of the composition the composition has less than 2% of the apparent volume of the product of pores having a size of less than 100 microns, and preferably the composition has less than 2% of the apparent volume of the product of pores having a size of less than 50 microns, and more preferably the composition has less 2% of the apparent volume of the product of pores having a size in the range, of 2 to 15

microns.

The dough-like material may subsequently be set and cured in a way generally known in the art to produce the finished product. This process may include pressing of the material and/or forming into a desired shape of product and may also include curing which may be effected in a humid atmosphere for example up to 100% relative humidity, and/or with the application of heat to the product. The curing may be effected in an autoclave and the temperature may be above 100°C; such a temperature is to be preferred when the cementitious composition contains the mixture of lime and silica as the hydraulic cement.

The cementitious composition may also comprise fibrous or textile reinforcement and in some applications it is preferred that the water-soluble polymer is also chemically cross-linked to the fibrous or textile reinforcement. It is preferred that the fibre is fibrillated polyethylene or polypropylene or a co-polymer of ethylene and propylene, such fibre having a secant elastic modulus of at least 10 GPa measured at 0.1% elongation.

The materials and processes described may be used, for example, to produce building products such as tiles, artificial slates, pipes and other moulded items for use in conditions exposed to natural weathering or water. The invention is particularly suitable for providing roofing elements or for cladding the exterior walls of buildings.

It is preferred that a cross-linking agent is used which is relatively stable at ambient temperature; it is to be understood that such a cross-linking agent enables the composition to be handled and processed without complications arising from cross-linking of the water-soluble polymer; the use of a cross-linking agent which is relatively stable at ambient temperature is particularly preferred for the production of the cementitious composition in accordance with this invention which contains the above defined ingredients (a), (b) and (d) and which merely requires the subsequent addition of an appropriate amount of water when the composition is to be used in the production of a hardened cementitious product.

It is preferred that the amount of cross-linking agent is stoichiometrically sufficient to react with all available sites within the polymer; however, lower quantities, for example 50%, or greater may also be used.

## EXAMPLES

The invention will now be described by way of example.

EXAMPLE 1

1000 grams of rapid hardening Portland cement were mixed with 10 grams of hydroxypropyl-methyl cellulose powder in a planetary mixer for one minute. 154 grams of a solution of 8.7 parts by weight of bis (2-hydroxyethyl) sulphone in 100 parts water were then added slowly to the mix while mixing continued. After two minutes of further mixing, the crumb which resulted was transferred to the almost closed nip of a two roll mill. As the mix became plastic the nip was gradually opened to about 4mm, at which time a continuous band of material had formed on the faster moving roll of the mill. This was removed by use of a doctor blade and pressed between smooth platens at 5 MPa and room temperature for 18 hours. The hardened sheet was then removed from the press and cured at 50 °C and 100% relative humidity for 16 hours. The sheet was then cut into test coupons 150mm x 20mm x 5mm and allowed to dry naturally at ambient conditions for 13 days. Some of the coupons were then immersed in water for 24 hours at room temperature. All coupons were tested by three-point bending and using the formula:

$$S = \frac{3 W l}{2 b d^2}$$

where S = flexural strength

W = breaking load

l = span between supports and centre loading point

b = width

d = thickness

the following results were obtained:

Dry strength = 38 MPa

Wet strength = 41 MPa

These may be compared with average value of 38 MPa for the dry condition and 36 MPa for the wet condition when the same procedure the composition was used but the sulphone was omitted.

The typical freeze-thaw test referred to is one in which the main cycle consists of maintaining the test pieces with one face in contact with water by placing on saturated foam rubber for 5 days while alternating the temperature from + 20 °C to - 20 °C twice a day thereby giving 10 cycles of freeze and thaw in this period.

During the alternating cycle, the temperature of -20 °C is maintained for 10 hours followed by +20 °C for 2 hours. The cooling from +20 °C to

-20 °C is effected in about 30 mins. and the heating from -20 °C to +20 °C is effected in about 30 mins.

This is followed by subjecting the test pieces to a temperature of 70 °C in air for 2 days at a low relative humidity. When subjected to the freeze-thaw test as defined above 100% of the samples were still intact after 60 of the main cycles whereas materials made in the same way without the addition of sulphone on average only exhibited 32% survival after this number of cycles.

The durability of these hardened compositions was further tested by subjecting test coupons to alternate wetting and drying. Once cycle consisted of immersion in water for 7 hours at room temperature, followed by drying at 70 °C for 16 hours and 1 hour cooling at ambient laboratory conditions. Samples of the material described above containing the sulphone cross-linking agent, in some instances, survived more than 60 cycles of the wet/dry cycling procedure, whereas samples of similar material made without sulphone failed by cracking after 7 cycles.

EXAMPLE 2

Example 1 was repeated but with 7.5 grams of hydroxypropyl methyl cellulose powder and 149 grams of a solution of 5.2 parts by weight of bis(2-hydroxyethyl) sulphone in 100 parts of water. Pressing time was 22 hours. When tested in three-point bending as defined in Example 1 the following results were obtained:

Dry strength = 38 MPa

Wet strength = 39 MPa

When subjected to the freeze-thaw test as defined above 100% of the samples were still intact after 60 of the main cycles whereas materials made in the same way without the addition of sulphone on average only exhibited 32% survival after this number of cycles.

EXAMPLE 3.

Example 1 was repeated but with a different cross-linking agent, namely 150g of a solution of 7.14 parts by weight 1,4 butandiol diglycidylether in 100 parts water. Towards the end of the planetary mixing stage 14g of a solution of 22.8 parts zinc fluoroborate in 100 parts water was blended into the crumb. The milled material was pressed for 17 hours at room temperature. When tested in three-point bending as defined in Example 1 the

following results were obtained:

Dry strength = 37 MPa

Wet Strength = 38 MPa

When subjected to the freeze-thaw test as defined above 100% of the samples were still intact after 40 of the main cycles whereas materials made in the same way without the addition of a cross-linking agent on average only exhibited 34% survival after this number of cycles.

When subjected to the wet/dry cycling test described in the above examples, samples of the material cross-linked with butandiol diglycidyl ether survived 30 cycles.

#### EXAMPLE 4.

Example 2 was repeated but with 2.5 parts by weight of chopped polypropylene fibre added during the mixing process on the roll-mill. The cured product was subjected to the wet/dry cycling test described in Example 1. This material cracked only after 66 cycles of this test whereas a similar fibre reinforced material in which the sulphone cross-linking agent had been omitted cracked within 54 cycles.

#### EXAMPLE 5

A material of the same composition described in Example 3, but with the addition of 2.5 parts by weight of chopped polypropylene fibre and processed in the manner described in Example 4 was subjected to the wet/dry cycling test described in Example 1. This material cracked only after 75 cycles which may again be compared with cracking within 54 cycles observed for similar material in which the cross-linking agent had been omitted.

#### EXAMPLE 6

Example 3 was repeated except that 150g of silica fume was added in place of an equal weight of cement and an additional 20g of water was added to render the mixture more workable. When tested in three-point bending as defined in Example 1 the following results were obtained:

Dry strength = 21 MPa

Wet strength = 27 MPa

#### Claims

1. An uncured cementitious composition which is free of isocyanates comprising in admixture:-
  - a) at least one hydraulic cement;
  - b) at least one reactive water-soluble polymer which is capable of providing a viscous solution in water at low addition levels;
  - c) water in an amount of from 10 to 25 parts by weight of water per 100 parts by weight of the cement; and
  - d) a water soluble cross-linking agent capable of effecting chemical cross-links between molecules of the said polymer in the presence of the cement and water.
2. A cementitious composition according to claim 1, wherein the reactive water-soluble polymer and the water-soluble cross-linking agent consist of at least one of the following pairs:-
  - (a) a cellulose ether plus a diepoxide;
  - (b) a cellulose ether plus a sulphone;
  - (c) a cellulose ether plus a compound containing labile chlorine;
  - (d) a cellulose ether plus ethylene imine;
  - (e) a carboxycellulose ether with polyvalent cation;
  - (f) polyacrylamide, or a derivative thereof or a copolymer of acrylamide plus a dialdehyde;
  - (g) polyvinylalcohol or partially hydrolised polyvinylacetate plus an inorganic acid;
  - (h) gelatin plus formaldehyde;
  - (i) polyacrylic acid or polyacrylic acid salt plus diexpoxide;
  - (j) a cellulose ether plus an acrylamide monomer, and a free radical initiator or heat;
  - (k) an allyl substituted cellulose ether plus a free radical initiator or heat.
3. A cementitious composition according to claim 2, wherein the composition comprises hydroxypropylmethyl cellulose and a diepoxide is 1,4 butanadiol diglycidyl ether, or butadiene diepoxide, or the diglycidyl ether of 1,2,3 propane triol, together with zinc fluoroborate catalyst.
4. A cementitious composition according to claim 2, wherein the composition comprises hydroxypropylmethyl cellulose and bis(2-hydroxyethyl)sulphone.
5. A cementitious composition according to any one of the preceding claims comprising blast furnace slag or pulverised fuel ash or a natural pozzolana or an artificial pozzolana.

6. A cementitious composition according to any one of the preceding claims which also comprises 5 to 20 parts by weight of fine particles of silica having a particle size distribution substantially between 0.005 microns (50 Å) and 0.5 microns. 5
7. A cementitious composition according to Claim 6, wherein the amount of silica is from 12 to 16 parts by weight. 10
8. A cementitious composition according to any one of the preceding claims which also comprises fibrous or textile reinforcement and in which said fibrous or textile reinforcement is chemically cross linked to the reactive water soluble polymer. 15
9. A method of making a hardened cementitious composition from an unhardened composition according to any one of the preceding claims, wherein the ingredients (a), (b), (c) and (d) are mixed to produce a uniform composition and the resulting composition is subjected to high shear mixing, preferably using a twin-roll mill or an extruder, in order to plasticise the composition to a dough-like or paste-like consistency, causing or allowing cross-links to form between the reactive water-soluble polymer and the cross-linking agent, and also subjecting the plasticised composition to vacuum conditions or to the application of pressure thereby to achieve substantial removal of voids so that the hardened composition has less than 2% of its apparent volume of pores having a size of less than 100 microns. 20 25 30 35
10. A method of making a hardened cementitious composition according to claim 9 whereby the hardened composition has less than 2% of its apparent volume of pores having a size of less than 50 microns. 40
11. A method of making a hardened cementitious composition according to claim 10, whereby the hardened composition has less than 2% of its apparent volume of pores having a size in the range of 2 to 15 microns. 45
12. The use of an unhardened composition as claimed in any one of claims 1 to 8 in making a roofing element such as a roofing tile or a cladding element for the exterior walls of buildings. 50

## Revendications

1. Composition pour ciment non traitée, qui est exempte d'isocyanates est caractérisée par un mélange comprenant :
  - a) au moins un ciment hydraulique,
  - b) au moins un polymère réactif soluble dans l'eau, qui est capable de fournir une solution visqueuse dans l'eau à faible niveau d'addition d'eau,
  - c) de l'eau en quantité de 10 à 25 parties en poids pour 100 parties en poids de ciment, et
  - d) un agent liant soluble dans l'eau capable de réaliser des liaisons chimiques entre molécules du polymère en présence de ciment et d'eau.
2. Composition pour ciment, selon la revendication 1, caractérisée en ce que le polymère réactif soluble dans l'eau et l'agent liant soluble dans l'eau se composent d'au moins l'une des paires suivantes :
  - a) un éther de cellulose plus un diépoxyde,
  - b) un éther de cellulose plus un sulfoné,
  - c) un éther de cellulose plus un composé contenant du chlore labile
  - d) un éther de cellulose plus de l'imine d'éthylène,
  - e) un éther de carboxycellulose avec cation polyvalent,
  - f) du polyacrylamide ou un de ses dérivés ou un copolymère d'acrylamide plus un dialdéhyde,
  - g) de l'alcool de polyvinyle ou de l'acétate de polyvinyle partiellement hydrolysé plus un acide inorganique,
  - h) de la gélatine plus de l'aldéhyde formique,
  - i) de l'acide polyacrylique ou un sel d'acide polyacrylique plus du diépoxyde,
  - j) un éther de cellulose plus un monomère d'acryl amide, et un radical libre initiateur ou de la chaleur,
  - k) un éther de cellulose substitué en allyle plus un radical libre initiateur ou de la chaleur.
3. Composition pour ciment selon la revendication 2, caractérisée en ce que la composition comprend de la cellulose hydroxypropylméthyle et un diépoxyde est de l'éther diglycidyl 1,4 butanadiol, ou du diépoxyde butadiène, ou de l'éther diglycidyl de 1, 2, 3 triol propane, ensemble avec du fluoroborate de zinc comme catalyseur.
4. Composition pour ciment selon la revendication 2, caractérisée en ce que la composition comprend de la cellulose hydroxypropylméthy-

- le et deux (2-hydroxyéthyle) sulfone.
5. Composition pour ciment selon l'une quelconque des revendications 1 à 4, caractérisée par du laitier de haut fourneau ou des cendres de combustible pulvérisées ou de la pouzzolane naturelle ou de la pouzzolane artificielle. 5
  6. Composition pour ciment selon l'une quelconque des revendications de 1 à 5, qui comprend de 5 à 20 parties en poids de particules fines de silice ayant une répartition de dimensions de particules substantiellement entre 0,005 microns (50 Å) et 0,5 microns. 10
  7. Composition pour ciment, selon la revendication 6, caractérisée par une quantité de silice de 12 à 16 parties en poids. 15
  8. Composition pour ciment selon l'une quelconque des revendications 1 à 7, caractérisée en ce qu'elle comprend aussi un renforcement fibreux ou textile et en ce que ce renforcement fibreux ou textile est chimiquement lié au polymère réactif soluble dans l'eau. 20
  9. Méthode pour la mise en oeuvre d'une composition pour ciment durcie à partir d'une composition non durcie, selon l'une quelconque des revendications 1 à 8, caractérisée en ce que les ingrédients (a), (b), (c) et (d) sont mélangés pour produire une composition uniforme et la composition résultante est soumise à un malaxage de grande efficacité, de préférence en utilisant un laminoir à double cylindres ou une extrudeuse, de façon à plastifier la composition en une consistance semblable à une pâte à pain ou à pâtisserie, occasionnant ou permettant la formation de liens étroits entre le polymère réactif soluble dans l'eau et l'agent liant, et aussi en assujettissant la composition plastifiée à des conditions de vide ou à l'application de pression, de façon à obtenir une substantielle suppression de vides et d'obtenir une composition durcie ayant moins de 2% de son volume apparent en pores de dimensions inférieures à 100 microns. 25
  10. Méthode selon la revendication 9 caractérisée en ce que la composition durcie a moins de 2% de son volume apparent en pores de dimensions inférieures à 50 microns. 30
  11. Méthode selon la revendication 10, caractérisée en ce que la composition durcie a moins de 2% de son volume apparent en pores de dimensions comprises entre 2 et 15 microns. 35

12. Utilisation d'une composition non durcie revendiquée dans l'une quelconque des revendications 1 à 8, caractérisée en ce qu'un élément de toiture est fabriqué comme une toiture en tuiles ou un élément de maintien pour les murs extérieurs de bâtiments. 40

## Ansprüche

1. Ungehärtete, von Isocyanaten freie, zementartige Zusammensetzung, die in Mischung enthält:
  - a) mindestens einen hydraulischen Zement;
  - b) mindestens ein reaktives wasserlösliches Polymer, das bei geringen Zugabemengen eine viskose Lösung in Wasser ausbilden kann;
  - c) Wasser in einer Menge von 10 bis 25 Gewichtsteilen Wasser auf 100 Gewichtsteile des Zements; und
  - d) ein wasserlösliches Quervernetzungsmittel, das chemische Quervernetzungen zwischen Molekülen des Polymers in Gegenwart des Zements und Wasser ausbilden kann.
2. Zementartige Zusammensetzung nach Anspruch 1, worin das reaktive wasserlösliche Polymer und das wasserlösliche Quervernetzungsmittel aus mindestens einem der folgenden Paare bestehen:
  - (a) ein Celluloseether plus ein Diepoxid;
  - (b) ein Celluloseether plus ein Sulfon;
  - (c) ein Celluloseether plus eine Verbindung, die labiles Chlor enthält;
  - (d) ein Celluloseether plus Ethylenimin;
  - (e) ein Carboxycelluloseether mit polyvalentem Kation;
  - (f) Polyacrylamid oder ein Derivat davon oder ein Copolymer von Acrylamid plus ein Dialdehyd;
  - (g) Polyvinylalkohol oder teilweise hydrolysiertes Polyvinylacetat plus eine anorganische Säure;
  - (h) Gelatine plus Formaldehyd;
  - (i) Polyacrylsäure oder ein Polyacrylsäuresalz plus Diepoxid;
  - (j) ein Celluloseether plus ein Acrylamid-Monomer und ein radikalischer Starter oder Wärme;
  - (k) ein Allyl-substituierter Celluloseether plus ein radikalischer Starter oder Wärme.
3. Zementartige Zusammensetzung nach Anspruch 2, worin die Zusammensetzung Hydroxypropylmethyl-Cellulose und ein Diepoxid, das 1,4-Butandiol diglycidylether oder Bu-

- tadiendiepoxyd oder der Diglycidylether von 1,2,3-Propantriol ist, zusammen mit einem Zinkfluorborat-Katalysator enthält.
4. Zementartige Zusammensetzung nach Anspruch 2, worin die Zusammensetzung Hydroxypropylmethyl-Cellulose und Bis (2-hydroxyethyl)sulfon enthält. 5
  5. Zementartige Zusammensetzung nach einem der vorhergehenden Ansprüche, enthaltend Gebläseofenschlacke oder pulverisierte Brennstoffasche oder eine natürliche Pozzolanerde oder eine künstliche Pozzolanerde. 10
  6. Zementartige Zusammensetzung nach einem der vorhergehenden Ansprüche, die auch 5 bis 20 Gewichtsteile an feinen Silicapartikeln enthält, die eine Partikelgrößenverteilung im wesentlichen zwischen 0,005 Mikron (50 Å) und 0,5 Mikron aufweisen. 20
  7. Zementartige Zusammensetzung nach Anspruch 6, worin die Silicamenge von 12 bis 16 Gewichtsteile ist. 25
  8. Zementartige Zusammensetzung nach einem der vorhergehenden Ansprüche, die auch Faser- oder Textilverstärkung enthält und worin die Faser- oder Textilverstärkung mit dem reaktiven wasserlöslichen Polymer chemisch quervernetzt ist. 30
  9. Verfahren zur Herstellung einer gehärteten zementartigen Zusammensetzung aus einer ungehärteten Zusammensetzung nach einem der vorhergehenden Ansprüche, worin die Inhaltsstoffe (a), (b), (c) und (d) gemischt werden, um eine gleichförmige Zusammensetzung zu erzeugen, und die resultierende Zusammensetzung einem Mischen bei hoher Scherung ausgesetzt wird, vorzugsweise unter Verwendung einer Doppelwalzenmühle oder eines Extruders, um die Zusammensetzung zu einer teigartigen oder pastenartigen Konsistenz zu plastifizieren, wobei die Bildung von Quervernetzungen zwischen dem reaktiven wasserlöslichen Polymer und dem Quervernetzungsmittel bewirkt oder erlaubt wird, und die plastifizierte Zusammensetzung auch Vakuumbedingungen oder der Anwendung von Druck ausgesetzt wird, um dadurch eine erhebliche Beseitigung von Hohlräumen zu erzielen, so daß die gehärtete Zusammensetzung weniger als 2% ihres scheinbaren Volumens an Poren aufweist, die eine Größe von weniger als 100 Mikron besitzen. 35  
40  
45  
50  
55
  10. Verfahren zum Herstellen einer gehärteten zementartigen Zusammensetzung nach Anspruch 9, wobei die gehärtete Zusammensetzung weniger als 2% ihres scheinbaren Volumens an Poren aufweist, die eine Größe von weniger als 50 Mikron besitzen.
  11. Verfahren zum Herstellen einer gehärteten zementartigen Zusammensetzung nach Anspruch 10, wobei die gehärtete Zusammensetzung weniger als 2% ihres scheinbaren Volumens an Poren aufweist, die eine Größe im Bereich von 2 bis 15 Mikron besitzen.
  12. Verwendung einer ungehärteten Zusammensetzung nach einem der Ansprüche 1 bis 8 bei der Herstellung eines Deckelementes wie etwa einem Dachziegel oder einem Verkleidungselement für die Außenwände von Gebäuden.